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Electrochemical Formation of CdSe Monolayers  
on the Low Index Planes of Au

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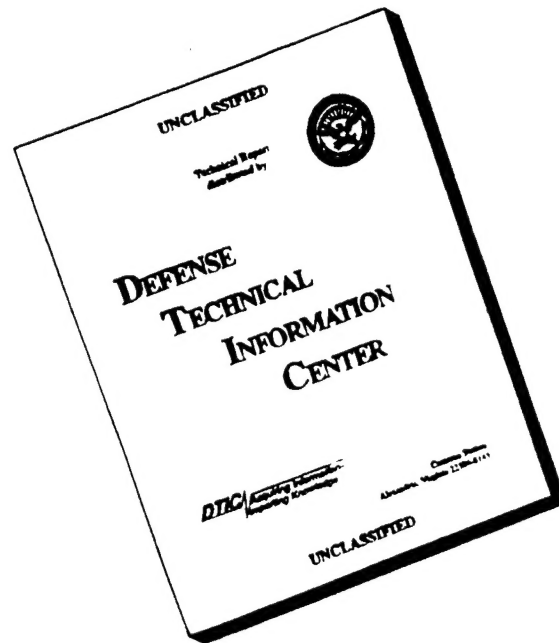
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# **ELECTROCHEMICAL FORMATION OF CdSe MONOLAYERS ON THE LOW INDEX PLANES OF Au**

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Key word: ALE, ECALE, UPD, CdSe, electrodeposition

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## ABSTRACT

The electrochemical analog of atomic layer epitaxy (ALE) is being studied. ALE is a method for growing thin films of materials using a cycle of surface limited reactions. The surface limited reactions control the deposition by limiting the growth to an atomic layer at a time. In electrochemistry, a surface limited deposition is generally referred to as underpotential deposition (UPD), and UPD is used to form the atomic layers in electrochemical ALE (ECALE). The work presented here is an atomic level study of the deposition of the first few monolayers of CdSe via ECALE: by the alternated UPD of atomic layers of Se and Cd on the low index planes of Au. UPD of Se resulted in the formation of ordered structures on each of the low index planes of Au, as observed by low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). The subsequent UPD of Cd resulted in CdSe deposits which exhibited 1:1 stoichiometry, as determined by coulometry and Auger electron spectroscopy (AES). The following LEED patterns were observed for the CdSe monolayers: Au(111)( $\sqrt{7} \times \sqrt{7}$ )R19.1°, Au(111)(3X3), Au(110)(2X3), and the Au(100)( $\sqrt{2} \times \sqrt{2}$ )R45°. Similar LEED patterns were observed on each surface for deposits formed using up to three ECALE cycles. *In situ* STM studies of Cd deposition on Se covered Au(111) indicated the formation of a (3X3) structure, consistent with LEED results, and with previous TEM studies by Golan et al.<sup>13</sup>. The same LEED patterns were also observed for CdSe monolayers where Cd was deposited as the the first atomic layer. AES indicated that the element deposited first remained on the bottom, and that deposited second remained on top.

## INTRODUCTION

Electrodeposition holds the promise of being a useful alternative for the growth of thin films of some compound semiconductors. This interest in electrochemical formation of compound semiconductor thin-films has resulted in well over 200 papers [1-4]. At present, the most wide spread compound electrodeposition method is codeposition, where both elements are reductively deposited from a single bath [5,6]. One of the drawback of this method, however, is a limited degree of control over the deposition process, as the only points of control are the potential, solution composition, and temperature.

In this group, electrodeposition of compound semiconductors is being studied by investigating the electrochemical analog of atomic layer epitaxy (ALE). In ALE, deposits are formed an atomic layer at a time, using surface limited reactions. In electrochemical ALE (ECALE) the same is true [7,8]. In electrochemistry, surface limited depositions are generally performed at underpotentials and are referred to as underpotential deposits (UPD) [9]. UPD is the deposition of a first element on a second, at a potential below that required to deposit the first element on itself. The driving force can be thought of as the free energy of formation of a surface compound.

In ECALE, the deposition takes place in a cycle, and each step in the cycle becomes a point of control. In stead of a single poitential controlling the deposition process, several may be used, at different steps. In addition, several solution are used, and the times allotted for various steps can be adjusted as well.

This paper presents an atomic level study of the ECALE formation of the first few monolayers of CdSe on the low index planes of Au. That is, CdSe monolayers are formed using UPD to control the deposition of each atomic layer. Investigations of the first ECALE cycle(s) are of increased importance, relative to succeeding layers, since a CdSe-Au heterojunction is formed. Studies of the first monolayer's deposition are then studies of a ternary system, and involve other considerations. One major concern is the lattice mismatch between the substrate and the depositing thin film. In order to form high

quality thin films, the lattice mismatch should be as low as possible to avoid lattice strain and the resulting defects [10]. Previous studies of CdTe deposition on Au, using ECALE, involved a 10% lattice mismatch [11,12]. A better match has been reported for CdSe depositing on Au(111), where the mismatch is reported to be only 0.6%, between twice the basal plane distance of CdSe and three Au-Au interatomic distances [13].

## EXPERIMENTAL

A Au "tri-crystal" was used in all experiments except those involving *in situ* STM. The Au tri-crystal consists of a single crystal polished on three faces, each to a different low index plane: (111), (110), and (100). This configuration allowed the structures formed on all three low index planes to be analyzed and compared in one experiment. A Au single crystal polished on two sides to the (111) plane was used for the *in situ* STM experiments. Each of the low index planes was oriented by Laue back reflection X-ray diffraction and subsequently polished on a two-axis goniometer (South Bay Technology). After mechanical polishing, the crystals were electropolished in a KCN solution at constant current [14].

The ultra-high vacuum electrochemical (UHV-EC) system used in this work has been described in other papers [15,16]. The main chamber houses facilities for Auger electron spectroscopy (AES) (Physical Electronics model #10-155) and low energy electron diffraction (LEED) (Physical Electronics model 15-120) as well as an ion bombardment cage for sample cleaning. A separate antechamber houses the electrochemical cell, allowing the electrode to be transferred without exposure to air. Prior to each UHV-EC experiment, the electrode was cleaned by Ar ion-bombardment, and annealing to remove surface damage. The Au(111) crystal used for STM experiments was cleaned in a methane/O<sub>2</sub> flame prior to each experiment.

Potentiostats were built in-house using conventional op-amp circuits. In all experiments, a Ag/AgCl (3M NaCl) (BAS model #MW 2021) reference electrode was used, and all potentials have been referenced to that electrode.

Solutions were purged with Ar or N<sub>2</sub> gas before electrochemical experiments. The Ar gas, used to back fill the antechamber of the UHV-EC instrument, was found to contain less than 2 ppm O<sub>2</sub>, as determined using a dedicated oxygen analyzer (Illinois Instruments model #2550). Selenium solutions were made from "puretronic" grade SeO<sub>2</sub> (Johnson Matthey) with a H<sub>2</sub>SO<sub>4</sub> supporting electrolyte (J.T. Baker Analyzed). Cadmium solutions were made from reagent grade CdSO<sub>4</sub> (Alpha), potassium acetate (J.T. Baker Analyzed), and acetic acid (J.T. Baker Analyzed). Some of the cadmium solutions used for voltammetric studies contained reagent grade Na<sub>2</sub>SO<sub>4</sub> as a supporting electrolyte (J.T. Baker Analyzed).

Coverages are reported versus the number of surface Au atoms, and were determined via coulometric stripping analysis. Surface roughness was accounted for by standardizing against known Se coverages (from LEED and STM measurements) for the low index planes. A roughness factor of 1.3 was calculated overall for the Au tri-crystal.

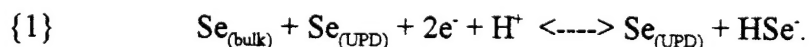
## **RESULTS AND DISCUSSION**

### **Formation of Se Atomic Layers**

The first step in the ECALE deposition of a II-VI compound has historically been the formation of a chalcogenide atomic layer, for a couple of reasons. First, the chalcogenides tend to be less air sensitive than the group II elements Cd and Zn, which are prone to oxidation. This makes the chalcogenide surface chemistry much easier to follow using UHV-EC and STM techniques. In addition, Cd is reported to form alloys with Au [17]. Formation of a chalcogenide atomic layer first may mediate Cd alloying.

The formation of Se atomic layers on Au(100) [18,19], Au(110) and Au(111) [20] have been described previously. Figure 1 shows a voltammogram of the Au tri-crystal in a solution containing 1 mM  $\text{H}_2\text{SeO}_3$ . In the cathodic sweep, starting at 0.6 V, the first peak in the voltammogram can be loosely termed as a Se "UPD" feature (peak  $\text{C}_1$ ), as the peak is surface limited and results in the deposition of less than a full monolayer of Se. The following peak,  $\text{C}_2$ , is also surface limited, but should probably not be considered a UPD peak, as more than 2 monolayers of Se are formed. On the return sweep, bulk Se is stripped from the surface beginning at 0.52 V (peak  $\text{A}_2$ ). The UPD Se is stripped in a separate feature (peak  $\text{A}_1$ ) above 0.6 V.

Three methods of forming Se atomic layers were studied in previous work [18,19]. Two of these methods were used in the experiments described here. For the most part, Se atomic layers were formed by scanning into peak  $\text{C}_1$ , unless the Se layer was deposited on an existing Cd layer. Cd is stripped at potentials corresponding to peak  $\text{C}_1$ , so that forming a Se atomic layer by deposition into  $\text{C}_1$  with Cd present on the surface, would result in the Cd stripping from the surface. To form Se atomic layers with Cd on the surface, then, reductive stripping of bulk Se was used. That method utilizes the equilibrium between Se and  $\text{H}_2\text{Se}$ :



Several monolayers of bulk Se are first deposited. The bulk Se is then reductively stripped from the surface in a solution which does not contain any  $\text{H}_2\text{SeO}_3$ . A Se atomic layer ( $\text{Se}_{\text{UPD}}$ ) remains on the surface because of its affinity for the Au or Cd covered surface. Atomic layer structures formed by Se on the Au low index planes have been studied using LEED, AES, and STM, and a summary of those results is shown in Table 1 [18-20].

**Table 1:** Table of Se coverages and structure formed on the low index planes of Au.

	LEED pattern	optimum coverage	observed by STM
Au(100)	(2X2)	1/4 or $(2.92 \times 10^{14})$	yes, 1/4
	(2X/10)	1/3 or $(3.90 \times 10^{14})$	yes, 1/3
	(/2X/2)R45°	1/2 or $(5.85 \times 10^{14})$	yes, 1/2
	(3X/10)-Se <sub>8</sub>	8/9 or $(1.04 \times 10^{15})$	yes, 8/9
Au(111)	(/3X/3)R30°	1/3 or $(4.50 \times 10^{14})$	yes, 1/3
	none	1 or $(1.35 \times 10^{15})$	(3Xn/3)- Se <sub>8</sub> , 1
Au(110)	(2X3)	2/3 or $(5.51 \times 10^{14})$	yes, 2/3

### Deposition of Cd on Se Atomic Layers

A voltammogram for Cd deposition on the clean Au tri-crystal is shown in Figure 2A. Cd UPD starts at 0.15 V in a broad wave that extends to about -0.1 V. There appears to be further Cd deposition after this peak, all the way into the bulk Cd deposition wave, at -0.7 V. The Cd UPD layer was not stable after emersion, as indicated by the AES spectrum in Figure 3C. The presence of O in the spectrum suggests that the Cd spontaneously reacted with the layer of solution coating the crystal after emersion (withdrawal from solution) and loss of potential control. Cd is thermodynamically unstable in water. Voltammetry for the UPD of Cd changed noticeably when a Se layer was first deposited, as shown in Figure 2B. Cd UPD begins 200 mV negative of where it does on a clean Au surface, and the peak is larger and sharper. The amount of Cd deposited in the UPD peak, was proportional to the amount of Se initially deposited. Unfortunately, the AES sensitivity factor for Se is extremely low, so that Se AES was not

used for quantitative purposes (Figure 3B). Very low O signals were observed for Cd UPD on Se atomic layers (Figure 3D), compared to those formed directly on Au (Figure 3C). When lower coverages of Se (below 1/2 ML), were present on the surface, oxygen levels were observed to increase, accordingly. Similar behavior was observed when Cd was deposited on low coverage Te structures [11,12]. Evidently, Cd bound to Se or Te is stabilized to oxidation upon emersion. Measurement of the Cd/Se ratios, obtained coulometrically, for a series of CdSe deposits where Cd was deposited at -0.4 V on top of different coverage Se atomic layers, resulted in three basic structure types (Figure 4). At low initial Se coverages (Figure 4A), deposits rich in Cd were formed, as a lack of Se resulted in the CdSe structure not completely covering the surface. Areas where CdSe did not form, however, were covered by Cd UPD, resulting in the high Cd/Se ratio. At Se coverages above 1/2, the deposits appeared stoichiometric, as sufficient Se was present to produce a complete layer of CdSe (Figure 4B). At still higher initial Se coverages, up to 2 monolayers, the Cd/Se ratio remained close to 1, indicating that the Cd reaction was not limited to Se at the surface, but interior Se atoms reacted as well (Figure 4C).

LEED was used to study CdSe deposits resulting from Cd UPD on 1/2 ML Se deposits. Two LEED patterns were observed on the Au(111) surface: at potentials near the onset of Cd deposition (between -0.15 V and -0.25 V), a  $(\sqrt{7} \times \sqrt{7})R19.1^\circ$  pattern was observed (Figure 5A), while deposition at potentials lower than -0.25 resulted in a (3X3) pattern (Figure 5B). Combinations of these patterns were also observed in the transition region, near -0.25 V. Both patterns were also observed in the formation of CdTe monolayers on Au(111) [11], however the  $(\sqrt{7} \times \sqrt{7})R19.1^\circ$  pattern was dominate in the CdTe deposition studies, while the (3X3) appears dominant in the present study. Structures proposed to account for the observed patterns and coverages are shown in Figures 6A and B. Figure 6A is a structure with a  $(\sqrt{7} \times \sqrt{7})R19.1^\circ$  unit cell and 3/7 ths coverage of both Cd and Se. The structure shown in Figure 6B has the (3X3) unit cell and 4/9ths coverage, slightly higher then for the structure in 6A (0.444 compared with

0.429) as expected since the (3X3) was formed at a lower Cd deposition potential. The (3X3) structure is consistent with previous TEM studies of electrodeposited CdSe nanoparticles, reported by Golan et al. [13]. The bulk structures of CdSe are Wurtzite and zinc blende, with Wurtzite being the thermodynamically preferred. At the one monolayer level, however, the two structures are indistinguishable from one another, and the structures shown in Figures 6A and B are consistent with both bulk structures.

A (2X3) LEED pattern was observed on a Se coated Au(110) surface after Cd deposition at -0.40 V (Figure 5C). This pattern was observed from the onset of Cd UPD at -0.20 V to potentials near bulk Cd deposition, -0.70 V. A proposed structure, Figure 6C, places the Se atoms in the troughs of the Au surface, with Cd atoms residing in the three fold hollow sites of the Se layer, at a coverage of 2/3 for both Cd and Se. The structure has a distorted hexagonal symmetry, where the CdSe distances are somewhat expanded in the [100] direction, across the Au troughs.

Poor quality LEED patterns were obtained for Cd deposition on Au(100). Figure 5D is a LEED pattern obtained after emersion from the Cd solution at -0.32 V. This pattern has  $\sqrt{2}$  beams, indicating a possible  $(\sqrt{2} \times \sqrt{2})R45^\circ$  structure. Other fractional order beams were sometimes observed, but were never captured well in photographs. These spots were in positions which, along with the  $\sqrt{2}$  spots, fit a  $(\sqrt{2} \times 2\sqrt{2})R45^\circ$  pattern. A proposed structure assuming a  $(\sqrt{2} \times 2\sqrt{2})R45^\circ$  unit cell is shown in Figure 6D. This structure is, again, quazi-hexagonal, with the distortion resulting from alignment with the Au(100) surface. A similar layer of CdS, electrodeposited on Au(100), was also observed to form a distorted hexagonal structure by Shannon and co-workers using STM [21].

In general, hexagonal or quasi-hexagonal monolayers of CdSe appear to have formed on each of the low index planes. This is consistent with the growth habit observed with X-ray diffraction (XRD) for thin CdSe films produced using ECALE. Figure 7 is an XRD pattern for a CdSe deposit formed on polycrystalline Au (vapor deposited on Si), using 200 ECALE cycles. Given that the structures formed on each of the Au low index

planes are so similar, it can be concluded that the crystallography of the Au substrate has little control over the resulting growth habit of the CdSe deposits.

### ***In situ* STM observations of CdSe formation on Au(111)**

Formation of the first monolayer of CdSe was also investigated using *in situ* STM, to try and follow the UPD of Cd on an initial Se atomic layer. Se atomic layers were first formed on a two-sided Au(111) crystal by reductive deposition at  $C_1$  (Figure 1). The crystal was then rinsed and mounted in the *in situ* STM cell [23], where the Cd solution was added. Figure 8A is an image of the surface at -0.10 V, positive of the onset of Cd deposition, and shows atomic resolution of the Se layer. Domains of a  $1/3$  coverage  $(\sqrt{3} \times \sqrt{3})R30^\circ$  hexagonal structure are evident along with domains of a structure composed of  $Se_8$  ring molecules. Descriptions of these two Se structures are reported elsewhere [18,19]. When the potential was then stepped into the Cd deposition region (-0.50 V), a hexagonal arrangement of atoms was observed (Figure 8B). The measured inter-atomic distances in this image (0.42 nm) agree well with the (3X3) structure proposed above (Figure 6B), and described by Golan et al. [13]. There also appears to be a number of clusters on top of the hexagonal array, a nm or two in diameter. The height of these features is between 0.15 to 0.20 nm. At present, they appear to be more CdSe, parts of a second layer. This is expected considering Figure 8A, where the majority of the surface is covered with the  $Se_8$  ring structure at a coverage of  $8/9$ ths, while the minority structure is the  $(\sqrt{3} \times \sqrt{3})R30^\circ$ , at a coverage of  $1/3$ . The ideal (3X3)-CdSe structure (Figure 6B) requires a Se coverage of  $4/9$ ths. Given this information, it is probable that upon completion of a monolayer of the (3X3)-CdSe structure, some Se would be left. The remaining Se should also react with Cd, as discussed above (Figure 4C), and result in formation of a partial second layer. If this interpretation is correct, it suggests that for Se to be used as the first atomic layer, great care should be taken to produce a very homogeneous deposit at  $4/9$ ths coverage for the first atomic layer of Se. It is also

interesting that the excess CdSe nucleates in such small clumps, homogeneously distributed across the surface. This appears to indicate very limited mobility for the Se while the Cd is depositing. It may further indicate that the CdSe does not nucleate at just a few sites, and then grow out. In that case, excess Se could get pushed to the side where it would react with Cd, producing a more in-homogeneous distribution of CdSe. That the excess Se, and thus CdSe, is evenly distributed, appears to indicate a very localized deposition process.

### **CdSe Formation Using Multiple ECALE Cycles**

In the preceding section, Se was formed by direct UPD of Se on Au from a  $\text{H}_2\text{SeO}_3$  solution at around 0.3 V. This method cannot be used to form Se atomic layers on deposits which contain Cd, as mentioned previously, due to the instability of the Cd at those potentials. Thus to form a second and successive monolayers of CdSe, Se atomic layers were formed by depositing two monolayers of bulk Se at -0.40 V, followed by reductive stripping of the excess in a 5 mM sodium borate solution for 2 minutes at -0.75 V. The Cd atomic layers were then deposited at -0.32 V. Figure 3E shows an AES spectrum of a deposit formed by this method. Note the ratio of Se/Cd remains similar to that obtained for one layer (Figure 3D), and the Au Auger peaks are further attenuated due to the presence of a thicker deposit. When three cycles were performed by this method, the Se/Cd ratio was again similar, but the Au peaks were totally absent. The rapid loss of the Au signal suggests that the deposit is probably growing in a layer by layer fashion. If the deposit was growing by a 3D nucleation mechanism, large areas of the surface would be relatively uncovered, and a Au AES signal would most likely still be evident, until the nucleated domains covered the surface. LEED patterns observed for the two and three cycle cases were similar to those for the single cycle case (Figure 5), but with increased diffuse intensity. The integral beams weakened after deposition of the 2nd

and 3rd layers, which is consistent with the substrate being shielded by the increasing film thickness.

### **Cd UPD as the First Atomic Layer**

As mentioned above, CdSe is usually formed by depositing Se as the first atomic layer. Several experiments were performed by first depositing an atomic layer of Cd on the clean Au, followed by an atomic layer of Se on top. Cd UPD was performed by scanning the potential from 0.30 V to -0.40 V (Figure 2A). The Se atomic layer was then formed by the reductive stripping method, using the same conditions described in last section. Figure 9 shows AES spectra for two CdSe deposits, one where the Cd was deposited first (Figure 9A) and one where the Se was deposited first (Figure 9B). In the "Cd first" deposit, the Cd AES signal is much smaller, suggesting that the Cd atoms remain on the bottom, in contact with the Au. That is, the Cd AES signal is dramatically attenuated by the layer of Se atoms on top. This configuration is supported by the stripping voltammetry (Figure 10). The stripping curve for the "Cd first" deposit is the dashed line and the "Se first" is the solid line. The integrated charge for Cd stripping in the Cd first deposit is only 7 % lower than the Se first deposit, certainly not enough to account for the discrepancy in the Cd Auger signals in Figure 9. The Cd stripping potentials for the Cd first deposit are shifted positive relative to the Se first deposit, indicating a difficulty in stripping, i.e. the Cd was buried below the Se. Similar behavior is seen in Figure 2C, for stripping a two monolayer thick CdSe deposit. That is, the potential needed to strip the last of the Cd, the interior Cd, was shifted positive of that needed to strip the top layer (Figure 2B). Similar behavior was also observe in stripping CdS deposits, formed with multiple ECALE cycles on polycrystalline Au [22].

LEED performed on the Cd first deposits, interestingly, produced similar patterns to those observed for the Se first deposits. This is further evidence that a specific CdSe

structures is forming on the surface, without regard to the sequence of deposition, the specific low index plane of the substrate, or the elemental coverages.

## CONCLUSION

Electrochemical formation of Se atomic layers has been previously investigated. Well ordered Se structures were seen to form on each of the low index planes Au. Cd UPD on these Se structures has been described above. The extent of Cd UPD proved to be proportional to the amount of the initially deposited Se, generally resulting in a stoichiometry of near 1:1 for initial Se coverages above 1/2 a monolayer. LEED indicated that ordered CdSe structures were formed on all three low index planes:

Au(111)( $\sqrt{7} \times \sqrt{7}$ )R19.1°-CdSe, Au(111)(3X3)-CdSe, Au(110)(2X3)-CdSe, and Au(100)( $\sqrt{2} \times \sqrt{2}$ )R45°-CdSe. Proposed structures for these CdSe monolayers all evidenced hexagonal or quazi-hexagonal structure, resembling a monolayer of the basal plane of CdSe. *In situ* STM studies of Cd UPD on Se covered Au(111) indicated a hexagonal structure with a (3X3) unit cell, consistent with LEED and the TEM results of Golan et al.<sup>13</sup>. Besides the (3X3) structure, there were 1 to 2 nm diameter clusters distributed homogeneously over the surface of the (3X3). These appear to be extra CdSe, formed because the initial coverage of Se was more than sufficient to form a single monolayer of CdSe on the surface. The extra Se was also converted to CdSe and began a second layer. These results appear to indicate that the deposition process is a distributed one, and is not limited to nucleation and growth at some small number of sites.

LEED patterns similar to those observe after deposition of a single monolayer of CdSe were observed for CdSe deposits formed using two and three ECALE cycles. The same ordered LEED patterns were also observed for CdSe deposits where Cd was the first element deposited, as well. In general then, a particular hexagonal CdSe structure

appears to form on the surface, independent of the initial substrate orientation or the element used to form the initial atomic layer.

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Figure 1 Voltammogram for the Au tri-crystal immersed in a solution of 1 mM  $\text{SeO}_2$  with 20 mM  $\text{H}_2\text{SO}_4$  supporting electrolyte. Scan rate = 5 mV/sec.

Figure 2 Voltammograms for the Au tri-crystal in a solution containing 1 mM  $\text{CdSO}_4$  with 10 mM  $\text{Na}_2\text{SO}_4$  supporting electrolyte and 1 mM acetate buffer, pH = 4.7. Scan rate was 5 mV/sec.

- A) After ion-bombarding and annealing (clean Au).
- B) After formation of a 1/2 coverage Se atomic layer.
- C) After formation of 1 Se monolayer.

Figure 3 AES Spectra taken on the Au(111) surface after the following treatments.

- A) After ion-bombarding and annealing (clean Au).
- B) After formation of a 1/2 coverage Se atomic layer.
- C) Cd UPD formed at -0.40 V on clean Au.
- D) One ECALE cycle of CdSe.
- E) Two ECALE cycles of CdSe.

Figure 4 Variations in surface composition as a function of the Cd/Se ratio:

- A) Initial Se coverage less than 1/2 ML
- B) Initial Se coverage near 1/2 ML
- C) Initial Se coverage greater than 1/2 ML

Figure 5 LEED patterns observed for CdSe deposition.

- A) Au(111)( $\sqrt{7}\times\sqrt{7}$ )R19.1°, electron energy 28.6 eV..
- B) Au(111)( $3\times 3$ ), electron energy 35.6 eV.
- C) Au(110)( $2\times 3$ ), electron energy 28.5 eV.
- D) Au(100)( $\sqrt{2}\times\sqrt{2}$ )R45°, electron energy 29.7 eV.

Figure 6 Proposed CdSe structures for one ECALE cycle.

(Au - white circles; Se - gray circles; Cd - black circles)

A) Au(111)( $\sqrt{7} \times \sqrt{7}$ )R19.1°

B) Au(111)(3X3)

C) Au(110)(2X3)

D) Au(100)( $\sqrt{2} \times \sqrt{2}$ )R45°

Figure 7 X-ray Diffraction pattern for a CdSe deposit formed on polycrystalline Au on Si, by 200 ECALE cycles. Spectra was taken at glancing incidence,  $\theta = 0.3^\circ$ .

Figure 8 *In situ* STM images of Au(111) covered with an atomic layer of Se.

A) Image taken at -0.10 V, prior to Cd deposition..

B) Image taken after stepping the potential to -0.50 V.

Figure 9 Auger Spectra of CdSe on Au(111) formed by:

A) Deposition of Cd UPD on clean Au followed by formation of an atomic layer of Se.

B) Deposition of a Se atomic layer followed by Cd UPD.

Figure 10 Stripping voltammograms in 20 mM H<sub>2</sub>SO<sub>4</sub> for CdSe deposits formed by:

Dashed Line: Deposition of Cd UPD followed by Se on that layer. Solid Line:

Deposition of a Se atomic layer followed by Cd UPD.

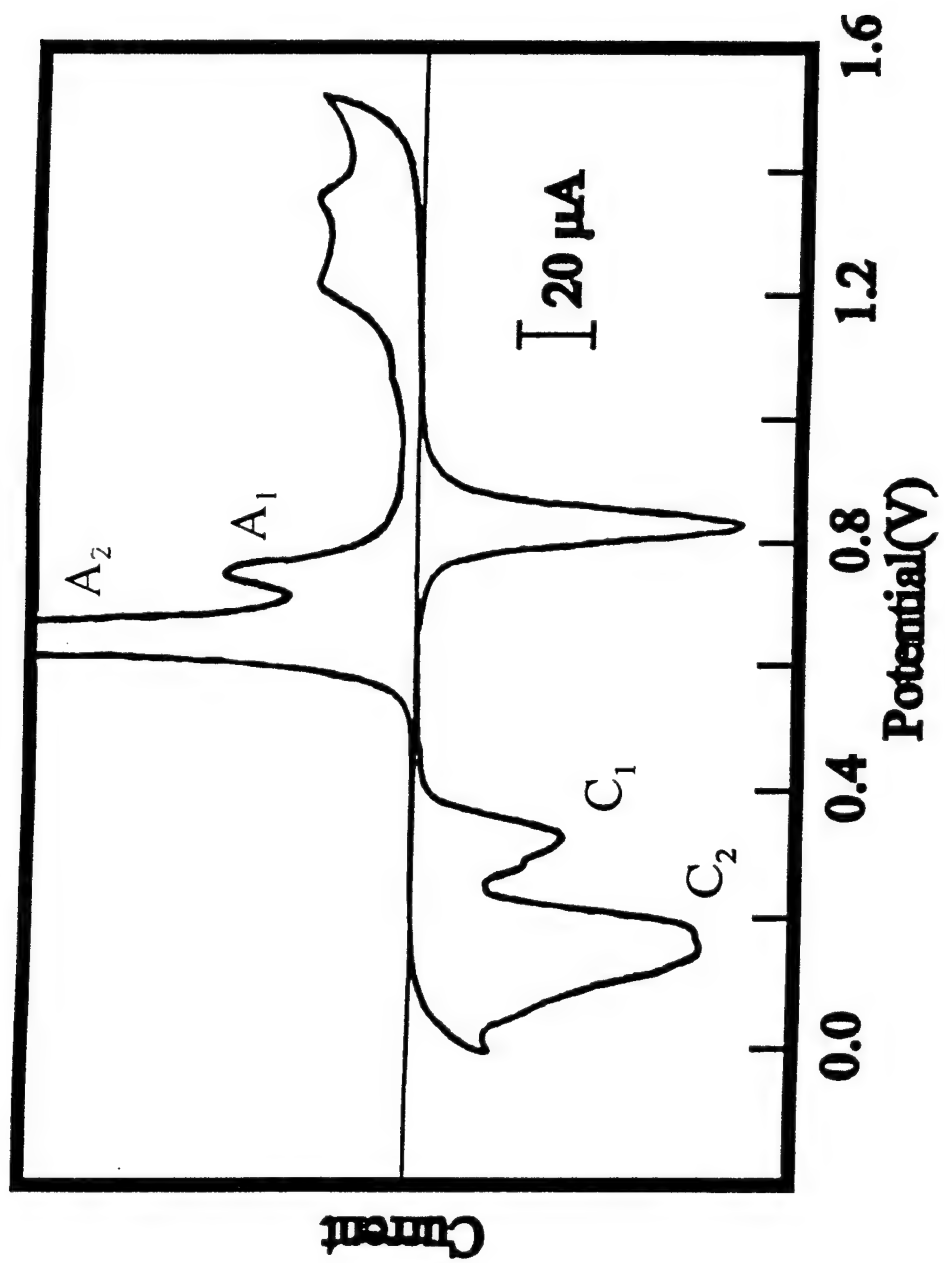
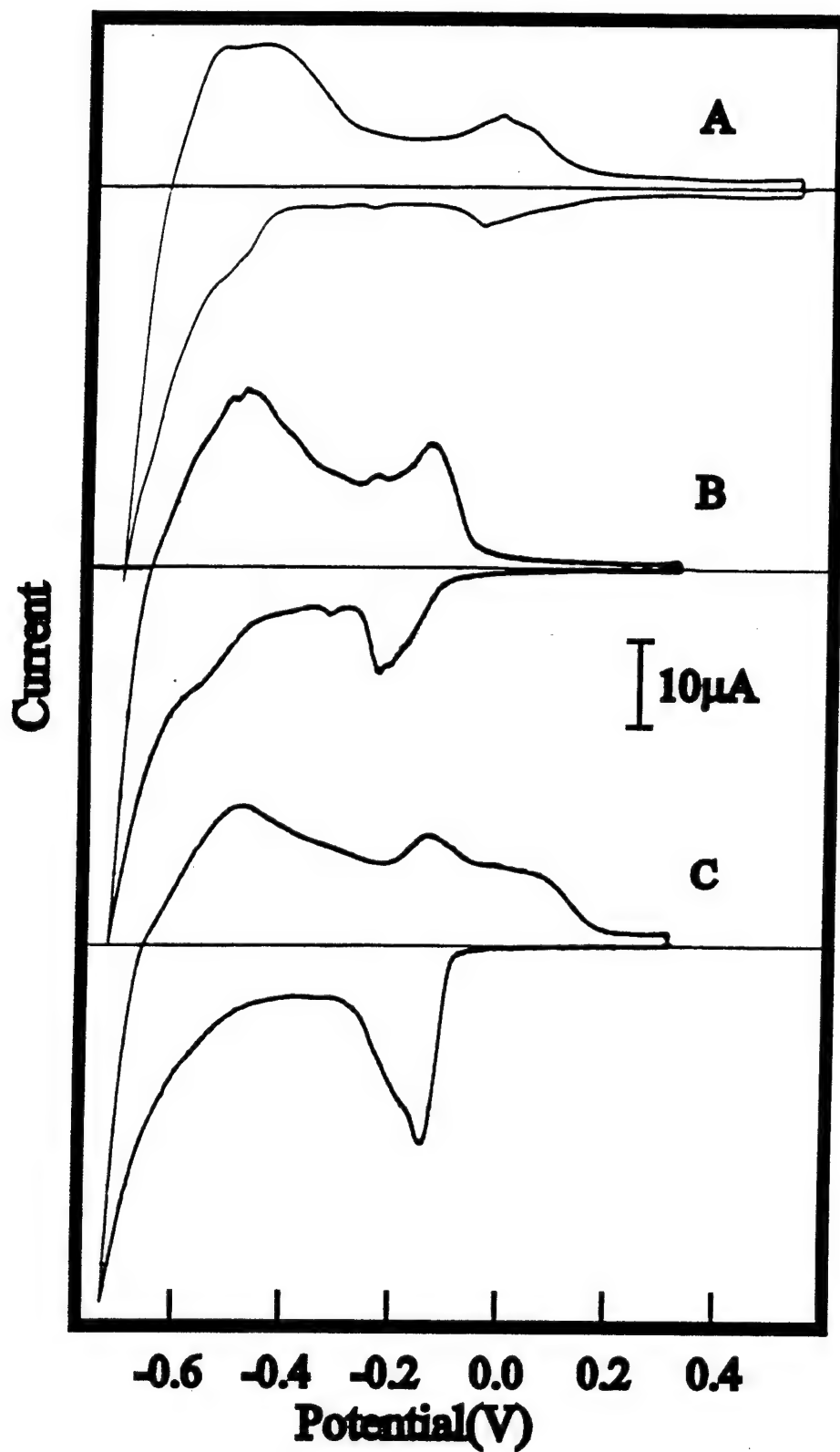


Figure 1  
Lishev et al.

Figure 2  
Liste et al.



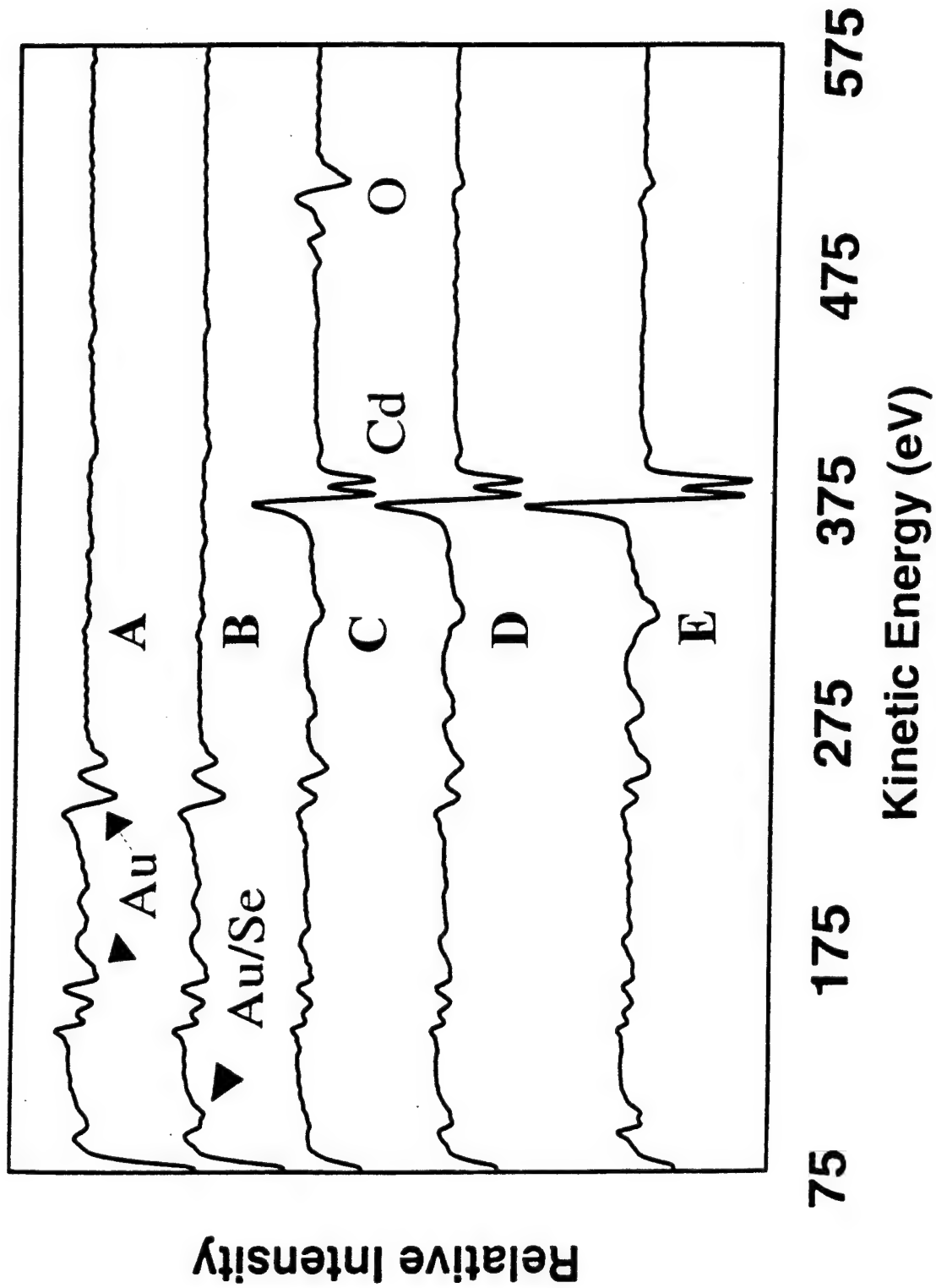


Figure 3  
Lischer et al.

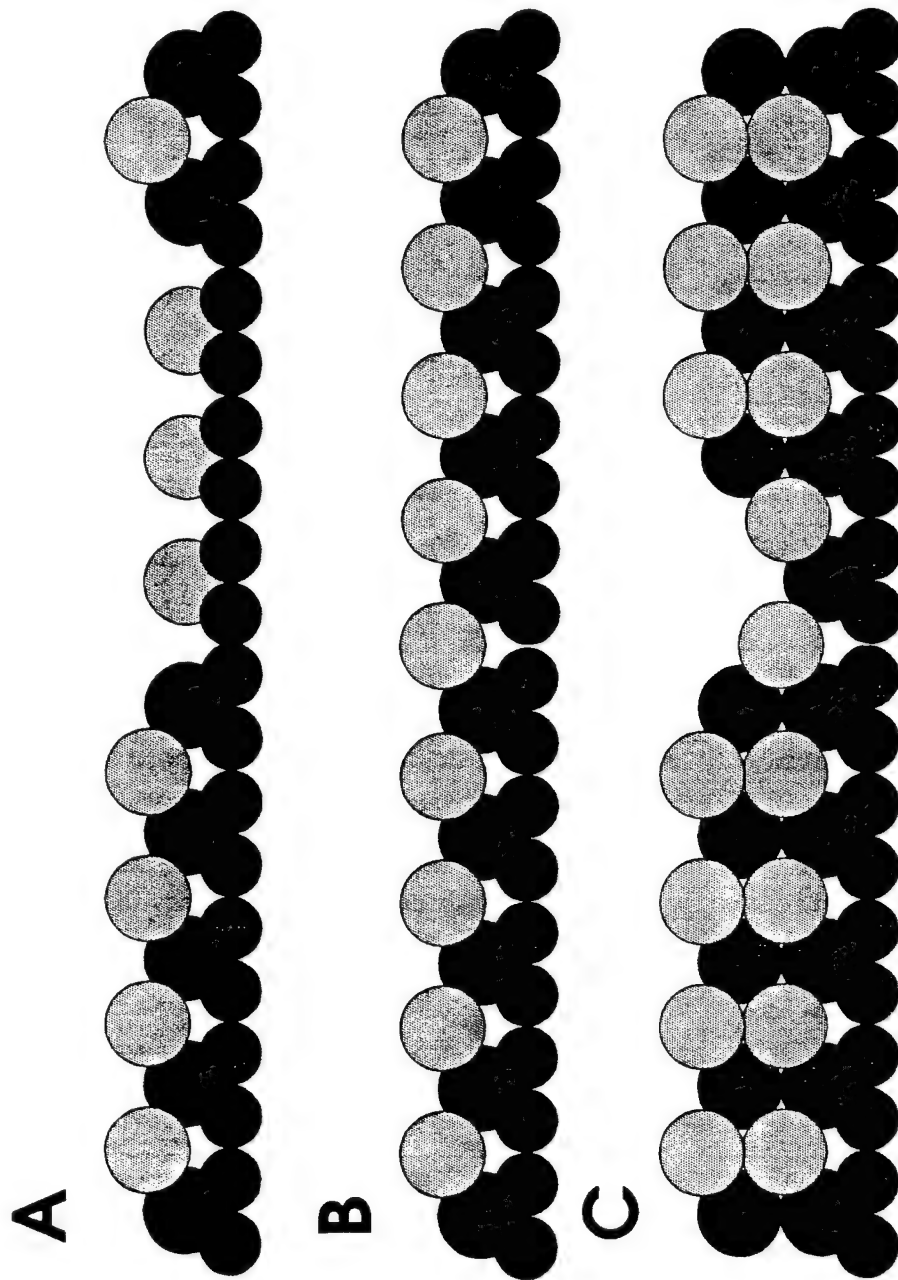


Figure 5A  
Lister et al.

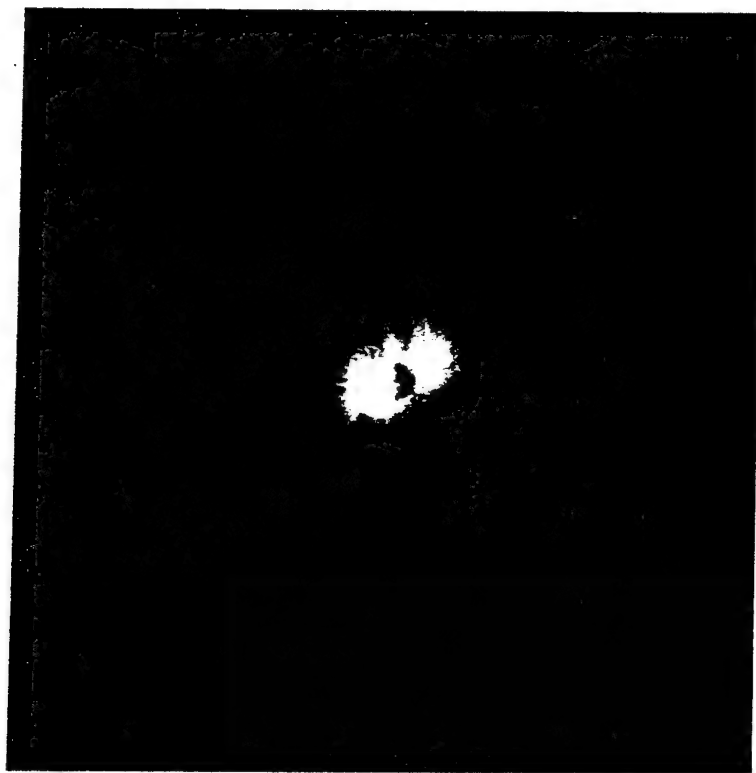


Figure 5B  
Lister et al.

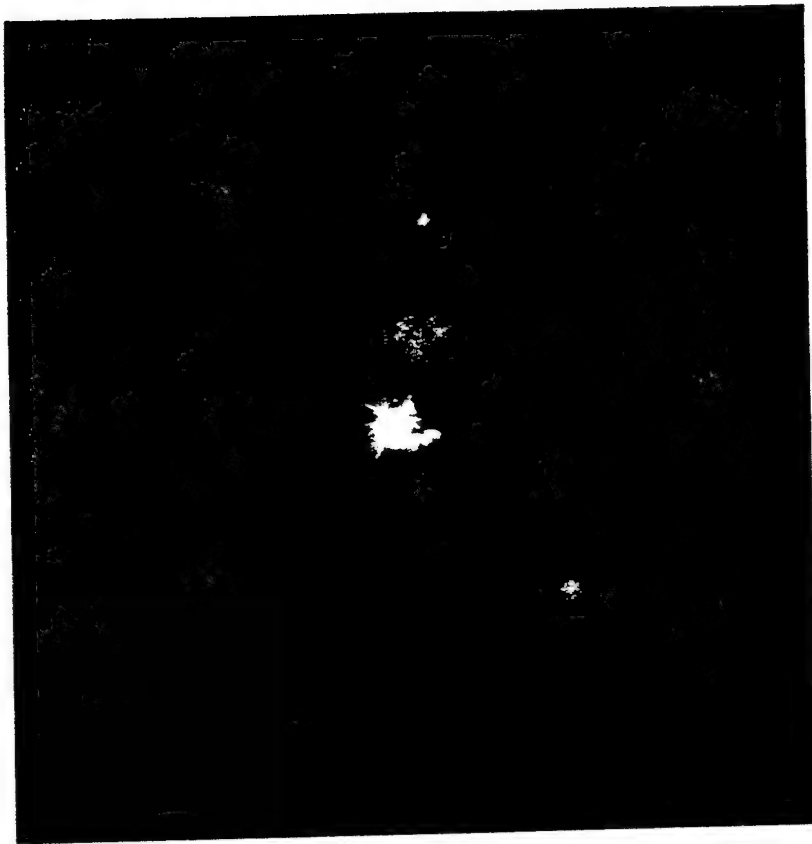


Figure 5C  
hister et al.

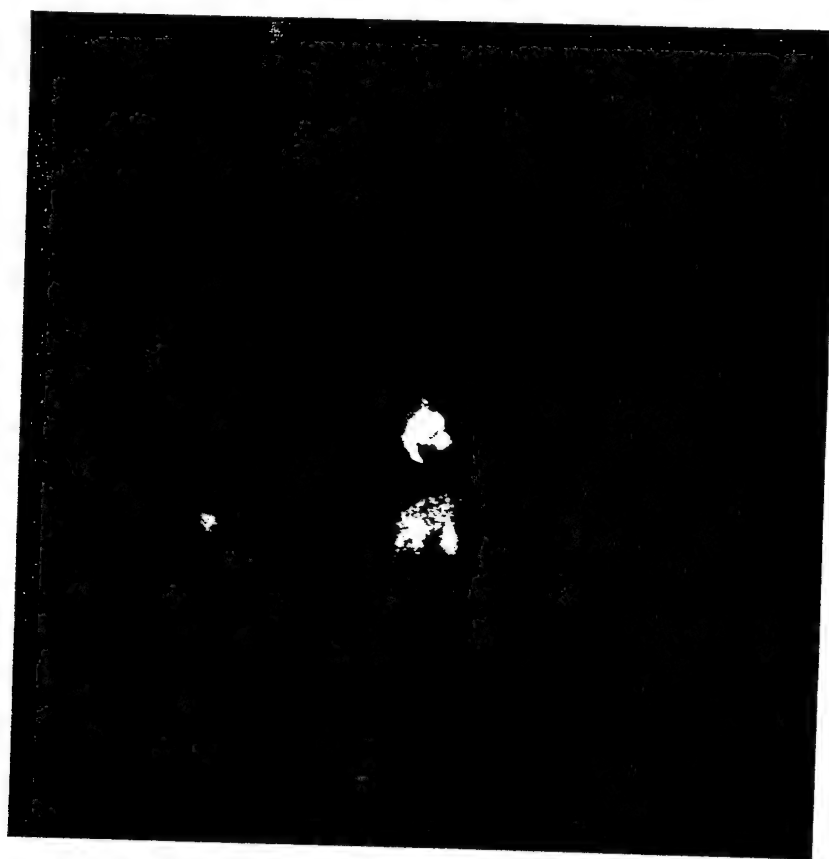


Figure 5D  
Hister et al.

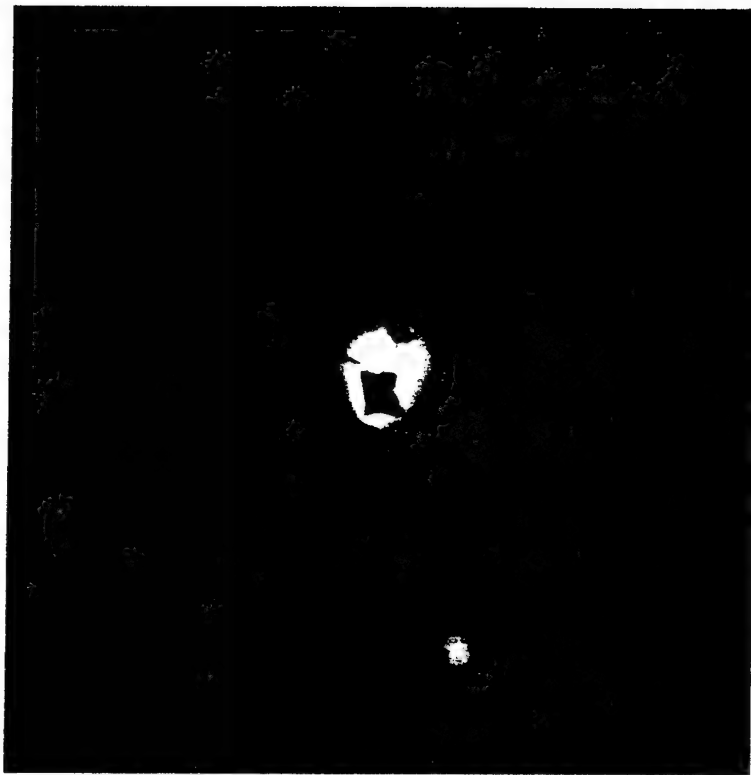
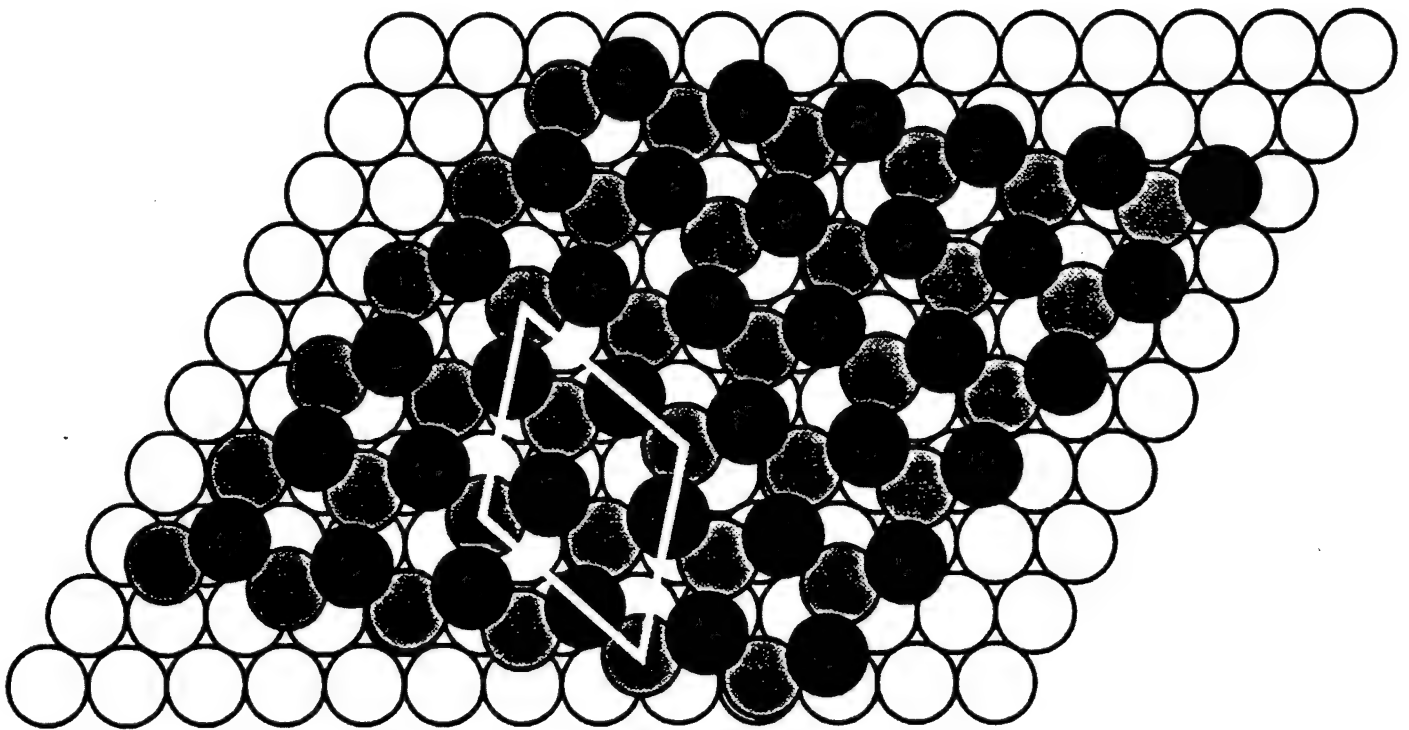


Figure 6 A  
Lister et al.

A



**B**

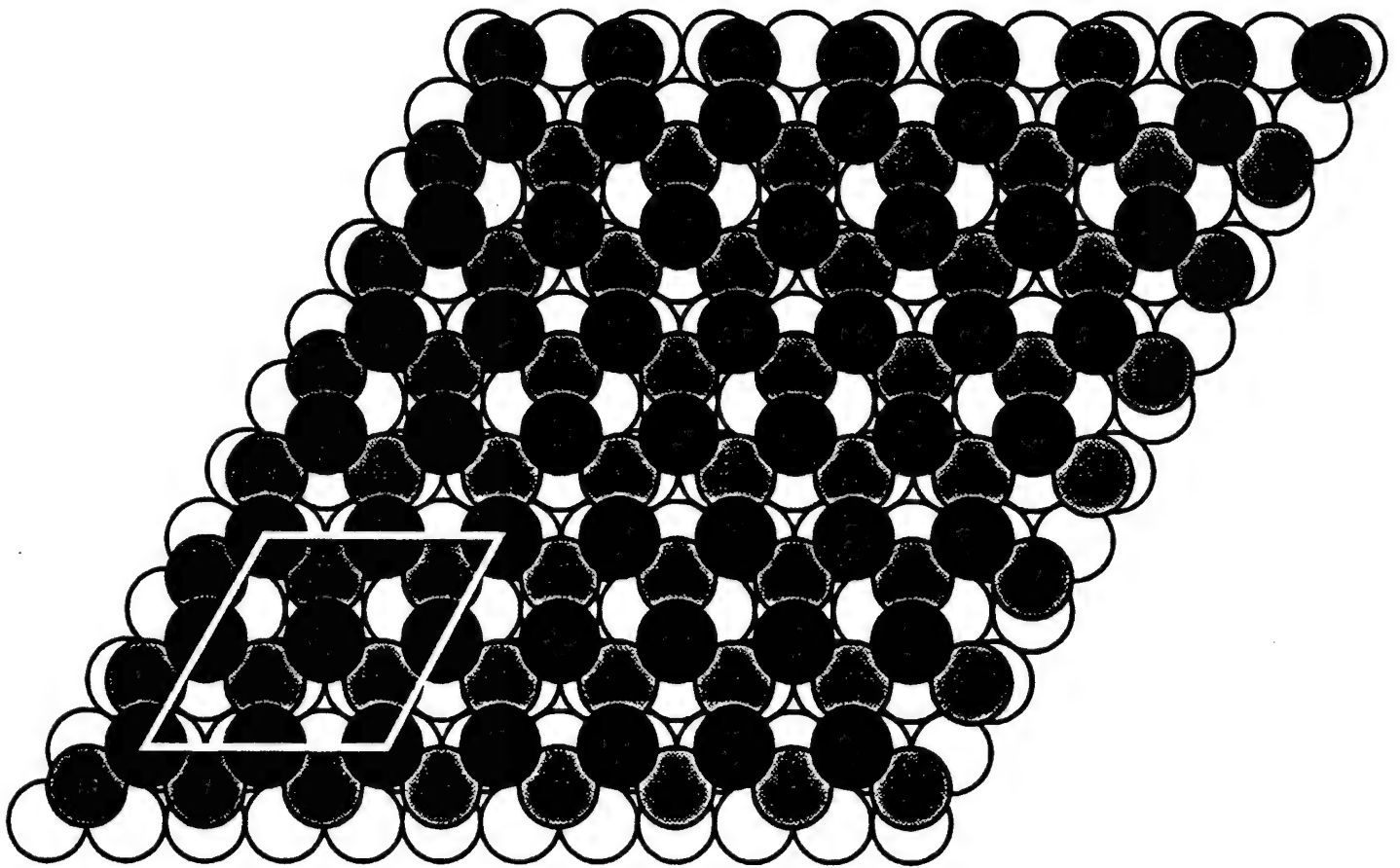
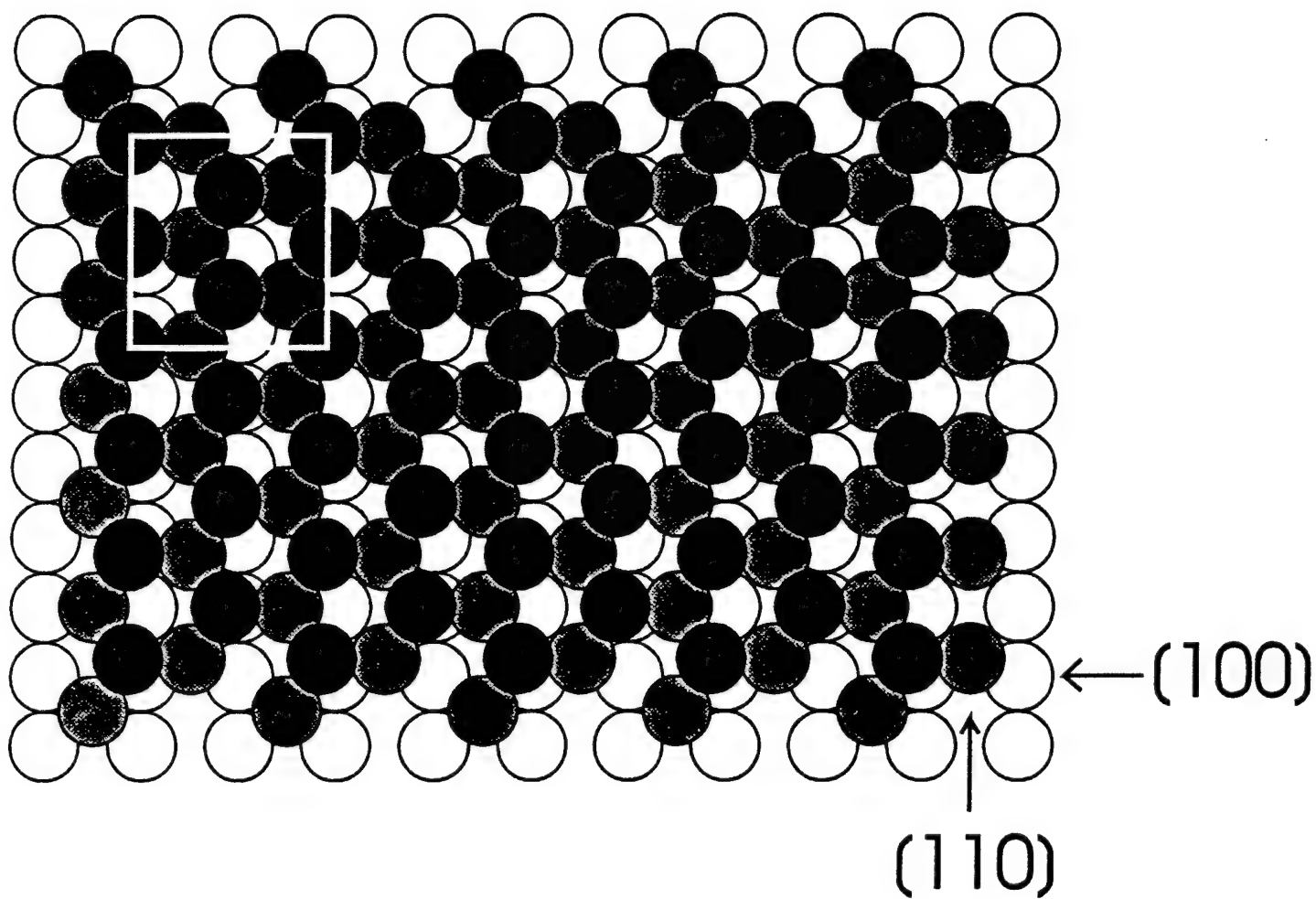
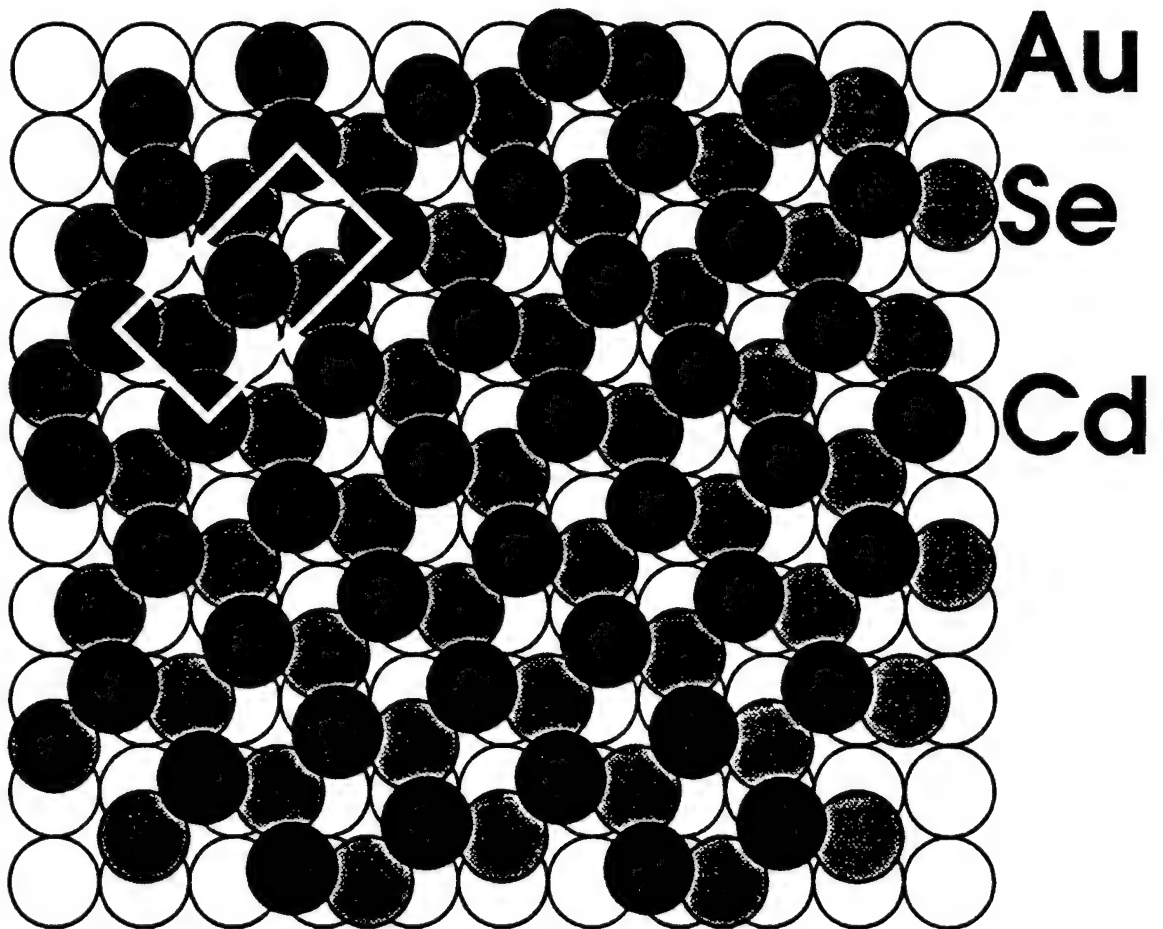


Figure 6C  
Lister et al.

C



D



# 200 CdSe ECALE Cycles

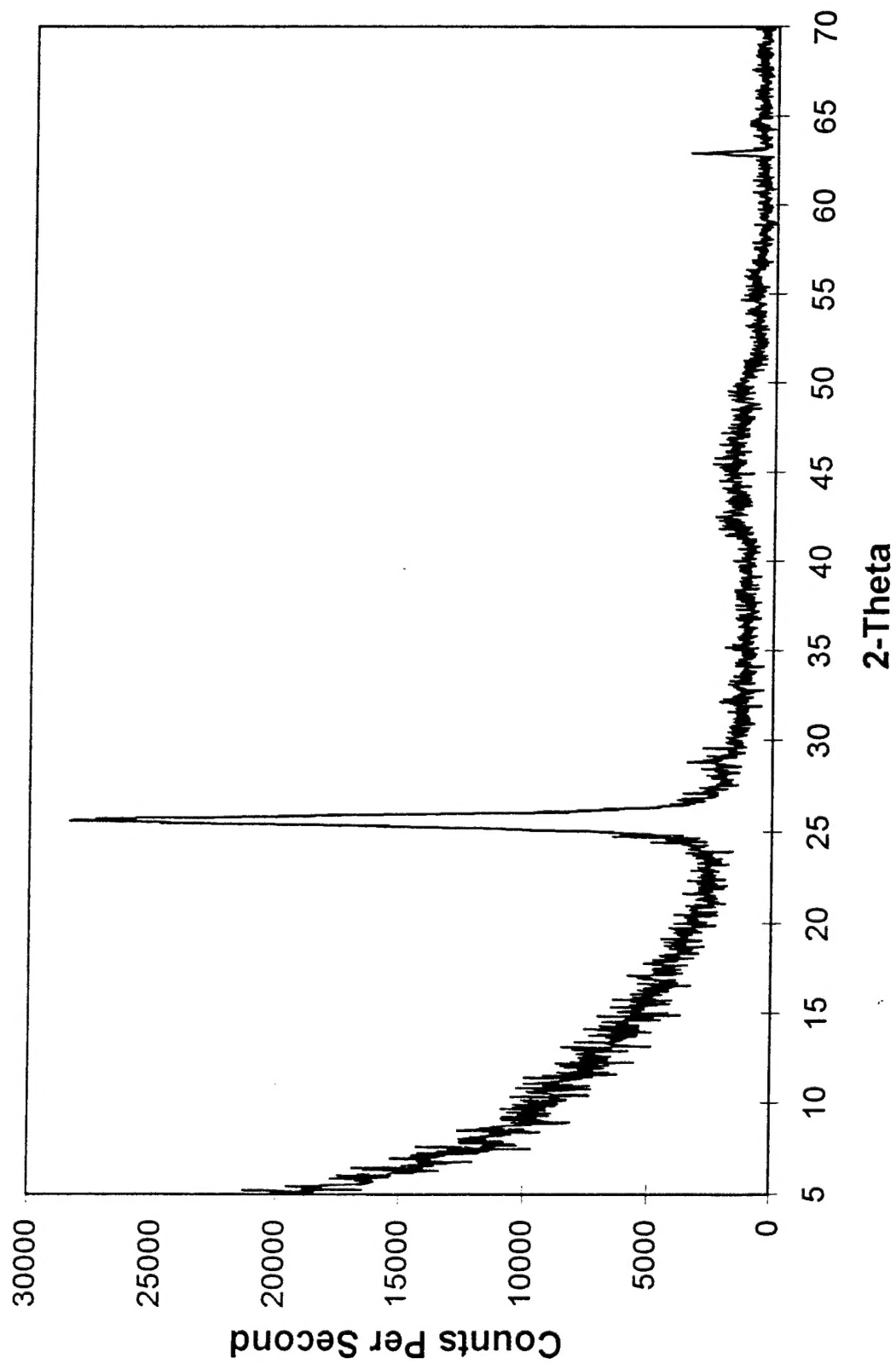
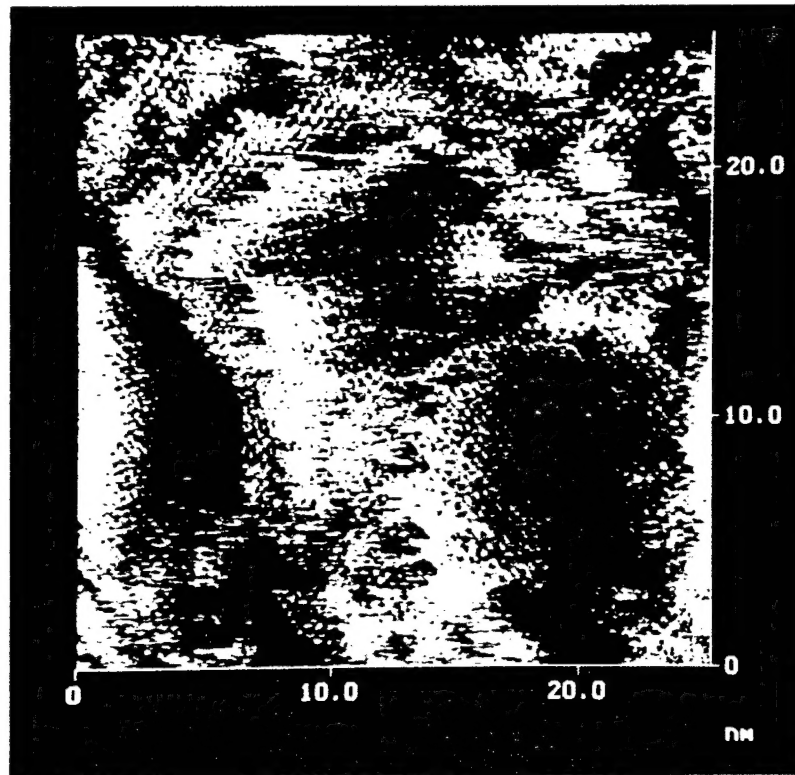
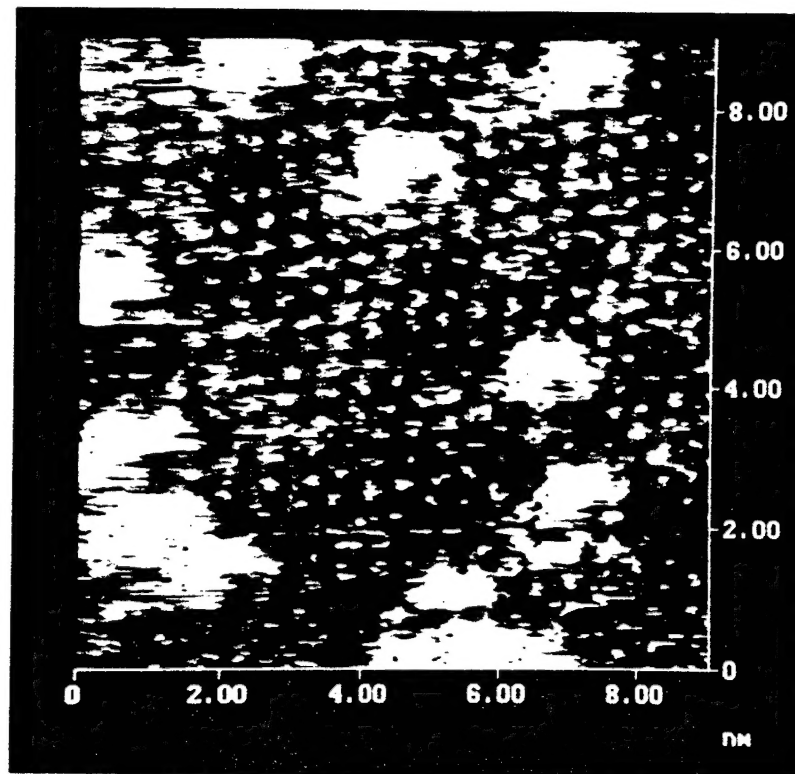


Figure 7  
Listu et al.

A



B



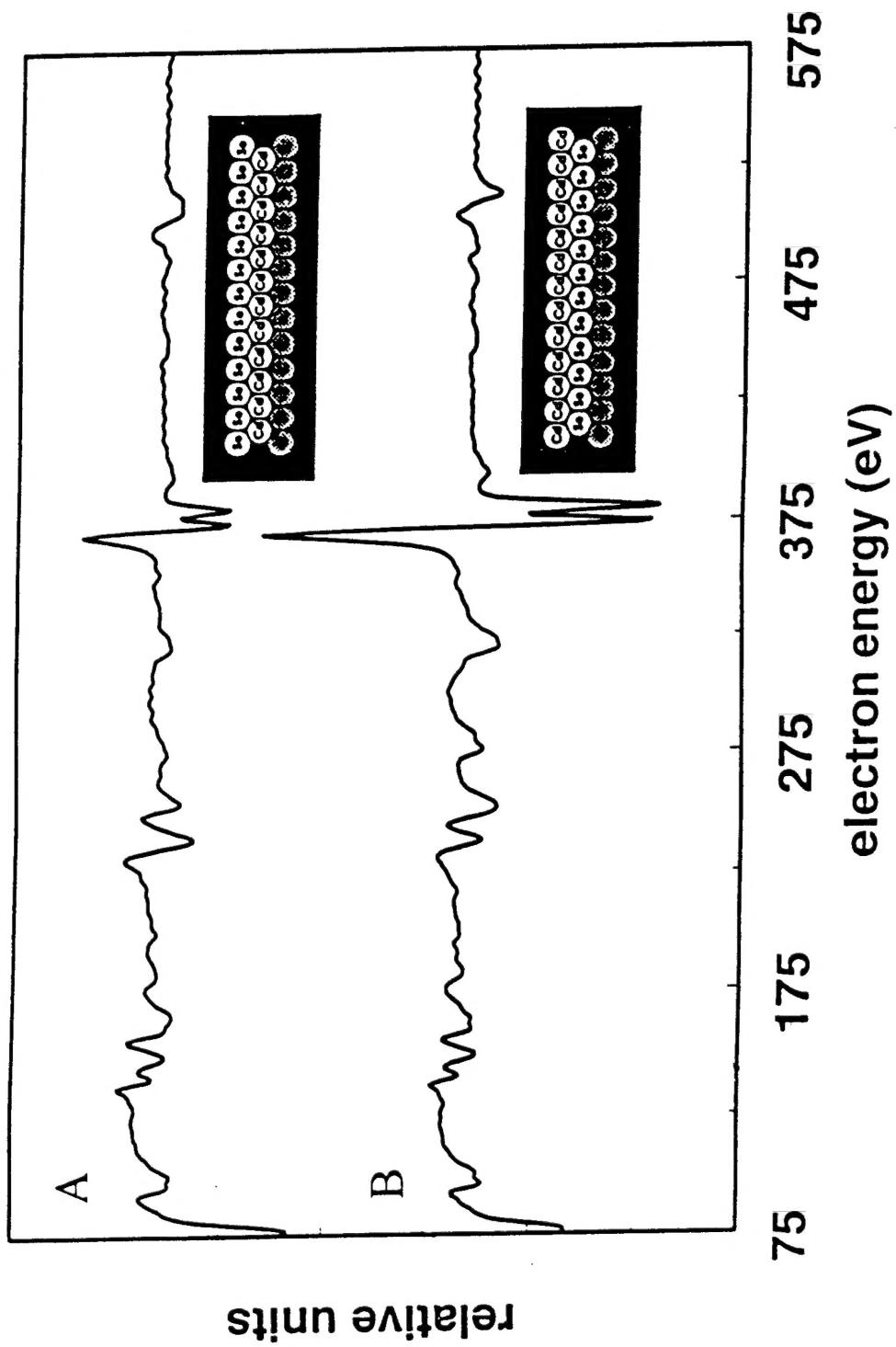


Figure 9  
Lishev et al.

Figure 10  
Lister et al.

